

# Real-time chemical analysis of root filling materials with heating

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**Real-time chemical analysis of root filling materials with heating; Guidelines for safe temperature levels.**

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3 **Real-time chemical analysis of root filling materials with heating; guidelines for safe**  
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5 **temperature levels.**  
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27 spectroscopy; warm obturation.  
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**Abstract:**

**Aim** To investigate the chemical changes affecting different types of gutta-percha and endodontic sealers during heating, and correlate changes with the heating capacity of different heat carriers.

**Methodology** The heating capacity of three endodontic heat carriers were evaluated using thermocouples to produce heat profiles. The devices were activated at different temperature set-ups, in continuous or cut-out modes. Chemical changes of six brands of gutta-percha and four types of sealers were assessed in real-time during heating using micro-Raman spectroscopy equipped with a heating stage. Raman spectra of each tested material were averaged and compared at different temperature levels. The sealers were further assessed by Fourier transform infrared (FTIR) spectroscopy.

**Results** None of the tested heat carriers achieved the temperature levels that were set by the devices and recommended by the manufacturer. The use of continuous heating mode resulted in higher rises in temperature than the 4s cut-out mode that reached 110 °C. The various brands of gutta-percha exhibited different chemical changes in response to heat. Some changes even occurred below temperature levels generated by the heating devices. All sealers revealed changes in their chemical composition upon heating. Changes in epoxy resin- and zinc oxide eugenol-based sealers were detectable at 100 °C, with structural alterations beyond that temperature and irreversible changes after cooling. Water loss was irreversible in BioRoot, but its chemical structure was stable as well as for the TotalFill.

**Conclusions** The heating capacity of endodontic heat carriers needs to be standardized, so that the temperatures delivered by the tips is the same as that set on the dial. Practitioners should be aware of the actual temperatures generated by these devices, and the suitability of sealers to be used at the temperature levels achieved.

## Introduction

Root canal filling aims to seal the root canal space after chemo-mechanical preparation to avoid microbial recontamination. For some time, gutta-percha has been the dominant root filling material (Ørstavik 2005). Many different techniques for using gutta-percha have been described, all of which involve using gutta-percha as a core material along with a flowable sealer to occupy unfilled spaces. Heat has been used to enhance the adaptation of solid gutta-percha within the complex root canal anatomy (Wu *et al.* 2002), in an attempt to improve the sealing quality of the root filling (Lea *et al.* 2005). During warm compaction, gutta-percha is heated inside the canal using heat carriers, which can be a hand instruments heated on a flame or an electronic device that generates heat and conveys it through metallic tips of various sizes.

Several studies have verified that the actual heat generated by carriers do not reach the set temperature on the equipment's dial (Silver *et al.* 1999, Venturi *et al.* 2002, Viapiana *et al.* 2015). This may be beneficial, as the high temperature levels recommended for warm compaction (180 °C - 200 °C) would be deleterious to the periodontium (Johnson *et al.* 2016). Heat may be further attenuated by the heat dissipation capability of teeth as well as endodontic sealers that further reduces the temperature conducted to surfaces of roots (Viapiana *et al.* 2014). This explains the minimal increase in the external root surface temperature by a few degrees above body temperature during heating (Venturi *et al.* 2002 Viapiana *et al.* 2015). Although some heat carriers were found to increase the root surface temperature up to 14.5 °C (Silver *et al.* 1999).

Regardless the widespread use of warm root filling techniques, the effect of heat on root filling materials has not been investigated extensively. Work by Schilder and colleagues (Schilder *et al.* 1974, Goodman *et al.* 1981, Schilder *et al.* 1985) reported the heat profiles of gutta-percha and temperatures of phase transformations with heating. It was established that gutta-percha was present in a  $\beta$ -phase below 49 °C that transformed into an  $\alpha$ -phase between 53-59 °C, after which it became amorphous. Upon rapid cooling, the material transformed directly into a  $\beta$ -phase without intermediate formation of an  $\alpha$ -phase and the material shrinks (Schilder *et al.* 1985). Differences in the thermal behaviour of different gutta-percha brands using differential scanning calorimetry has been reported

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3 (Roberts *et al.* 2017). Roberts *et al.* (2017) reported that gutta-percha was stable during warm vertical  
4 compaction contrary to Maniglia-Ferreira *et al.* (2008) who suggested the break-down of gutta-  
5 percha's molecular structure.  
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9 The effect of heat on endodontic sealers is not well documented. A rise in the temperature to 100 °C  
10 has been reported to result in degradation of epoxy resin-based sealers and evaporation of water from  
11 calcium silicate-based sealers (Viapiana *et al.* 2014, Viapiana *et al.* 2015, Camilleri 2015, Atmeh &  
12 AlShwaimi 2017). The duration of heat application was also found to affect the stability of sealers  
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18 (Atmeh & AlShwaimi 2017).  
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20 This study aims to correlate the heating capacity of several endodontic heating devices with changes  
21 in the chemical structure of different brands of gutta-percha and endodontic sealers upon heating.  
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23 From this data, recommendations for the range of temperature levels tolerated by root filling materials  
24 can be used with the devices tested during warm compaction techniques.  
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## 30 **Materials and Methods**

### 31 *Heat profiles of endodontic carriers*

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33 Three endodontic heat carriers were tested: E&Q Master (Meta Biomed, Chalfont, PA, USA),  
34 SuperEndo B&L (B&L Biotech, Gyeonggido, Korea), and System-B (Sybrondental, Orange, CA,  
35 USA). The E&Q Master was supplied with fine/fine-medium heating tips and could be operated at  
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180 °C and 230 °C with automatic cut-out after 4 seconds. SuperEndo B&L was operated at 230 °C  
using tips with three tapers (0.06, 0.08, 0.10) and size 55 heating tip. System-B was set at 200 °C and  
heating tips with 0.06, 0.08, 0.10, or 0.12 tapers were used.

The temperature generated by each heat carrier was recorded using K-type thermocouples (2 mm  
diameter, Maplins, Birmingham, UK) at 2 mm, 8 mm and 16 mm from the tip of the carrier. The  
thermocouples were connected to a multi-channel data logger (PicoData Logger, TC-08, St Neots, UK)  
and fixed into a 3 mm thick Perspex plate to ensure reproducibility and intimate contact with the heating  
tip. Prior to measurements, the heating carriers were acclimatized to 37 °C (Hybaid Shake and Stack  
Oven, Thermoscientific, Loughborough, UK) (Fig.1). Temperatures were recorded in real-time at a rate  
of 1s<sup>-1</sup> for 112s using the PicoData logging software. The heat profiles generated by the devices were

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3 measured over 3 cycles of heating (4 seconds) and cooling (30 seconds). Devices with continuous  
4 heating mode option (SuperEndo B&L and System-B) were activated for 30 seconds then left to cool.  
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6 The measurements were repeated 3 times and their average was calculated and plotted.  
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#### 9 *Assessment of root filling materials during heating*

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11 Six brands of gutta-percha were tested; ProTaper Universal (PTU) and ProTaper Next (PTN)  
12 (Mailliefer Instrument Holding, Ballaigues, Switzerland), Wave One (WO) (Dentsply Mailliefer,  
13 Ballaigues, Switzerland), Wave One GOLD (WG) (Dentsply Tulsa Dental Specialties, Tulsa, OK,  
14 USA), thermo-plasticized injectable gutta-percha (TPI), and 2% standardized points (STD) (Sure  
15 Dent Corp, Gyeonggi-do, Korea). The four sealers assessed were epoxy resin-based AH Plus  
16 (Dentsply International, Addlestone, UK), zinc oxide eugenol-based Pulp Canal Sealer (Kerr, Orange,  
17 CA, USA), and two calcium silicate-based TotalFill BC Sealer (FKG Dentaire, La Chaux-de-Fonds,  
18 Switzerland), and BioRoot RCS (Septodont, Saint-Maur-des-Fossés, France).  
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#### 28 -Raman Spectroscopy

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30 The materials were placed separately on a glass slide inside a heating chamber attached to a Surface  
31 Enhanced Raman Scattering (SERS) Spectroscopy (LabRAM HR EVO, Horiba Scientific, Kyoto,  
32 Japan). Imaging was performed using a 688nm Helium Neon laser beam of 11 mW power with a 600  
33 grooves/mm diffraction grating and a 50x/0.75 NA (numerical aperture) objective lens at room  
34 temperature. Gutta-percha samples were heated gradually from 30 °C to 200 °C at a 10 °C/min rate  
35 and the spectra acquired at 30, 40, 50, 60, 70, 80, 100, 150, and 200 °C temperatures. Sealers were  
36 heated to 200 °C at a rate of 30 °C/min and the spectra acquired at 25, 50, 75, 100, 125, 150, 175 and  
37 200 °C temperatures. An additional spectrum (cooled) was acquired for each sample after cooling  
38 down to room temperature after 30 minutes.  
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49 Acquired Raman spectra were uploaded into spectral analysis software (SpectraGryph-1.0, available  
50 at [www.effemm2.de/spectragryph/](http://www.effemm2.de/spectragryph/)), and peaks of interest were determined and compared for each  
51 material at each temperature. To analyse changes in gutta-percha, the integrated intensity ratio was  
52 measured as a ratio between each peak's area to a reference peak (105 cm<sup>-1</sup>) in the same spectrum.  
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54 Both Raman peaks at 105 cm<sup>-1</sup> and 311 cm<sup>-1</sup>, which represent barium sulfate and zinc oxide  
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3 respectively (Fig.2-d), were considered as internal standards due to their thermal stability within the  
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5 temperature levels used in this study.

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7 To identify irreversible changes, the integrated intensity ratios of peaks were plotted as percentages to  
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9 the intensity of same peaks at 30 °C using the following formula:

$$11 \quad \text{Percentage of Change} = \left( \frac{I_x - I_{30}}{I_{30}} \right) \times 100\%$$

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15 Where ( $I_x$ ) is the integrated intensity of the peak at 200 °C or after cooling, while ( $I_{30}$ ) is the intensity  
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17 of the same peak at 30 °C. The change after cooling was considered reversible if it did not exceed the  
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19 range between the highest and lowest levels measured for the control peak (311 cm<sup>-1</sup>) at any  
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21 temperature in each material.

#### 22 23 -Fourier Transform Infrared Spectroscopy

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25 The sealers were also investigated using Fourier Transform Infrared (FT-IR) by attenuated total  
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27 reflectance spectroscopy (FT-ATR). A smart MIRacle ATR accessory (ThermoFisher Scientific,  
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29 Waltham, MA, USA) was attached to a Nicolet 6700 spectrometer (ThermoFisher Scientific, Waltham,  
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31 Massachusetts, USA) with a liquid nitrogen cooled, high-speed, high sensitivity mercury cadmium  
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33 telluride (MCT) detector. The standard diamond crystal plate was replaced with a MIRacle heated  
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35 diamond plate attached to a control module (Pike Technologies, Fitchburg, WI, USA). The spectrometer  
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37 was set to measure between 650 cm<sup>-1</sup> and 4000 cm<sup>-1</sup> at a resolution of 16, scans to average of 2 and data  
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39 spacing of 1.928 cm<sup>-1</sup> at each measurement in absorbance mode. Background spectra were collected  
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41 and stored at room temperature (21 ± 1 °C). Sealers were mixed and/or dispensed following  
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43 manufacturers' instructions and were placed onto the ATR plate ensuring the diamond crystal (3 mm  
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45 diameter) was positioned centrally within a ring 16 mm internal diameter. A baseline measurement was  
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47 taken immediately after sample placement at room temperature (21 ± 1 °C) and then the heating module  
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49 was activated to heat the samples at a rate of 12.5 °C/min. Measurements were taken from 25 °C to 200  
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51 °C at increments of 25 °C and then air-cooled to 25 °C and re-measured. All spectra were baseline  
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53 corrected between 650-4000 cm<sup>-1</sup> and an average (n=3) was taken. The testing assembly was kept high  
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55 relative humidity.  
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## Results

### *Heat profiles of endodontic carriers*

The heat profiles of tested heat carriers with different tips are shown in Fig.3. None of the devices reached the selected temperature shown on their display, which was below 60 °C in the 4s cut-out mode regardless of the temperature setting (Table-1). There was no specific pattern in the change of temperature in relation to the size, taper or location of the tips. The E&Q Master could only be operated in the cut-out mode and set at 180 °C (Fig.3-a) or 230 °C (Fig.3-b). Although the maximum temperature with the 230 °C selection was higher than with 180 °C, the actual temperature did not exceed 60 °C in both. The highest temperature generated by SuperEndo at 230 °C in cut-out mode was 60 °C (Fig.3-c) compared with 110 °C achieved in the continuous mode (Fig.3-d). System-B generated heat below the set level at 200 °C. The highest temperature was 55 °C in the cut-out mode (Fig.3-e) and 65 °C in the continuous mode (Fig.3-f).

### *Root filling materials and heating*

#### - Gutta-percha

The Raman spectra of gutta-percha at 30 °C are shown in Fig.2-a, with peaks assignment in the Table in Fig.2-d. The percentage of change in the intensity of each peak after heating to 200 °C or cooling compared to peaks at room temperature is shown in Fig.2-b. The integrated intensity ratios of peaks are plotted at each temperature in Fig.2-c, and their pattern of change can be compared to the control peak (311 cm<sup>-1</sup>). Upon cooling, all changes in the intensities of peaks in PTU were within the limits of change in the internal standard and were not persistent after cooling (Fig.2-b). This also applied to PTN and WO, except for the peak at 350 cm<sup>-1</sup> that changed differently after 70 °C and 50 °C, respectively, and did not recover after cooling. (Fig.2-b, c). In WG, many peaks changed differently than the control peak above 100 °C, however, only the peak located at 1670 cm<sup>-1</sup> did not recover after cooling. Most peaks in TPI changed similar to the control peak except the peaks at 350 cm<sup>-1</sup> and 2885 cm<sup>-1</sup> above 70 °C. The change was persistent in the peak at 350 cm<sup>-1</sup> only. Cooling STD to room temperature was associated with an increase in the intensity of most peaks. Changes were all

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3 reversible except for the peaks at  $1284\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$ , which exhibited changes above  $80\text{ }^{\circ}\text{C}$   
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5 (Fig.2-c).  
6

#### 7 8 - Endodontic Sealers

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10 The Raman and FT-IR spectra of endodontic sealers at different temperatures are plotted in Fig.4.  
11  
12 Heating the epoxy resin-based sealer above  $100\text{ }^{\circ}\text{C}$  caused a noticeable drop in Raman peaks at  $780$   
13  $\text{cm}^{-1}$ ,  $1260\text{ cm}^{-1}$ ,  $2850\text{ cm}^{-1}$ ,  $2873\text{ cm}^{-1}$ ,  $2924\text{ cm}^{-1}$ ,  $3010\text{ cm}^{-1}$  and  $3087\text{ cm}^{-1}$  (Fig.4-a). The intensities of  
14  
15 peaks did not recuperate after cooling, which indicates irreversible changes. In the FT-IR spectra,  
16  
17 bands located at  $1293\text{ cm}^{-1}$ ,  $1233\text{ cm}^{-1}$ ,  $1362\text{ cm}^{-1}$ ,  $1503\text{ cm}^{-1}$ ,  $1650\text{-}2120\text{ cm}^{-1}$  all dropped gradually  
18  
19 with heating but recovered after cooling. The peak at  $900\text{ cm}^{-1}$ , however, dropped remarkably after  
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21  $100\text{ }^{\circ}\text{C}$  and did not recover after cooling.  
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24  
25 After cooling, the Raman (Fig.4-c) and FT-IR (Fig.4-d) spectra of the zinc oxide eugenol-based sealer  
26  
27 were totally different than the spectra during heating. Raman peaks at  $385\text{ cm}^{-1}$ ,  $480\text{ cm}^{-1}$ ,  $799\text{ cm}^{-1}$   
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29  $^{\circ}$ ,  $1450\text{ cm}^{-1}$ ,  $1616\text{ cm}^{-1}$ ,  $1649\text{ cm}^{-1}$ ,  $2873\text{ cm}^{-1}$  and  $2938\text{ cm}^{-1}$  dropped remarkably at temperatures  
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31 above  $125\text{ }^{\circ}\text{C}$ , while peaks at  $1151\text{ cm}^{-1}$  and  $1190\text{ cm}^{-1}$  dropped above  $150\text{ }^{\circ}\text{C}$ . The FT-IR spectra  
32  
33 showed a drop in the bands located at  $740\text{ cm}^{-1}$ ,  $790\text{ cm}^{-1}$ ,  $1146\text{ cm}^{-1}$ ,  $1608\text{ cm}^{-1}$ ,  $1695\text{ cm}^{-1}$  after  $100$   
34  
35  $^{\circ}\text{C}$ , while new peaks appeared at  $1400\text{ cm}^{-1}$ ,  $1430\text{ cm}^{-1}$  and  $1536\text{ cm}^{-1}$  at the same temperature level.  
36

37  
38 Heating the premixed calcium silicate-based sealer (TotalFill) resulted in a drop in several peaks in its  
39  
40 Raman and FT-IR spectra. However, all these changes were reversible and recovered upon cooling  
41  
42 (Fig4-e, f). FT-IR peaks at  $1972\text{ cm}^{-1}$ ,  $2026\text{ cm}^{-1}$ ,  $2335\text{ cm}^{-1}$ ,  $2362\text{ cm}^{-1}$ ,  $2550\text{ cm}^{-1}$ , and  $3400\text{ cm}^{-1}$   
43  
44 dropped reversibly above  $100\text{ }^{\circ}\text{C}$ . Heating of BioRoot resulted in flattening in the FT-IR bands at  
45  
46  $1650\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  above  $100\text{ }^{\circ}\text{C}$ , which persisted after cooling. No changes were detectable in  
47  
48 the Raman spectra however (Fig4-g, h).  
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#### 51 52 **Discussion**

53  
54 Although phase transformation of gutta-percha occurs at around  $60\text{ }^{\circ}\text{C}$ , many of the available heat  
55  
56 carriers are programmed at  $200\text{ }^{\circ}\text{C}$  or above. Conversely, the actual temperature achieved by heating  
57  
58 devices was reported to be much lower than the reading displayed on their dial (Silver *et al.*1999,  
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3 Venturi *et al.* 2002, Viapiana 2014). This discrepancy is confirmed by this study as the range of  
4 temperatures recorded was 33-110 °C although the devices were set at temperatures 180-230 °C  
5 (Fig.3). The maximum temperature level that was used during the Raman and FT-IR imaging was 200  
6 °C, which is much higher than the actual temperature generated by most heat carriers. Such  
7 temperature levels are unfoundedly recommended by endodontic textbooks (Glickman & Walton  
8 2009, Johnson *et al.* 2016) and hence it was used here. The duration of heat application is another  
9 factor that varies among clinicians. Prolonged heat application may endanger tissues and may affect  
10 the integrity of sealers (Atmeh & AlShwaimi 2017). Using heat carriers in continuous mode without  
11 automatic cut-out would risk prolonged heating and higher temperature levels (Fig.3-d, f).

12  
13 It must be pointed out that the laboratory setup used to examine the chemical changes affecting tested  
14 root filling materials might be different than the clinical situation. The temperatures recorded in heat  
15 carriers were monitored at 37 °C, which may potentially change when the tips of the heat carriers are  
16 used inside a root canal. Despite data being available on the heat generated at the external root surface  
17 (Silver *et al.* 1999; Venturi *et al.* 2002, Viapiana *et al.* 2014, 2015), heat conducted to the inner root  
18 surface has not been well reported. A study measuring these temperatures in real-time during root  
19 canal filling (Donnermeyer *et al.* 2017) may not be representative as sealers would have come in  
20 contact with the thermocouples and affected their reading. Although using dentine as a substrate may  
21 seem more relevant to the clinical situation, sealers were examined on glass slides or metal plates,  
22 which was a necessity to evaluate the samples in the testing devices. However, this may not affect the  
23 results as changes affecting the root filling materials were being investigated while the heating tips  
24 were in direct contact with materials, which is the exact situation in the clinic. Acquiring data in real-  
25 time during heating meant that the samples were heated for longer durations in comparison with the  
26 situation in the clinic. However, the results reported here were comparable to previous results where  
27 short heating was used (Atmeh & AlShwaimi 2017).

28  
29 Raman spectroscopy has been a useful method to study chemical changes in polymers, therefore it  
30 was valuable to investigate the impact of heat on root filling materials. However, Raman data must be  
31 interpreted cautiously, as several factors might confound the results (Robinson *et al.* 2014). Using an  
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3 internal standard as a reference to verify changes in the intensities of peaks is desirable (Michielsen  
4 2001), henceforth two of stable constituents of gutta-percha were used; barium sulphate and zinc  
5 oxide (Mohazzabi & Seacry 1976). Raman spectra obtained for different gutta-percha brands  
6 confirmed their basic composition (Fig.2-d) (Freidman *et al.* 1975, Gurgel-Filho *et al.* 2003). Slight  
7 differences in their spectra may reflect differences in their molecular weight, crystallinity, and the  
8 percentage of their components (Goodman *et al.* 1974). This may explain variations in their thermal  
9 behaviour and response to heat (Fig.2-b) (Roberts *et al.* 2017).

10  
11 Despite the different crystallographic structures of the  $\alpha$ - and  $\beta$ -phases of gutta-percha, differences  
12 have been reported in their Raman spectra at 990  $\text{cm}^{-1}$ , 1211  $\text{cm}^{-1}$ , 2896  $\text{cm}^{-1}$ , and 2914  $\text{cm}^{-1}$  (Pathak *et al.*  
13 2006). After cooling, the spectra of gutta-percha were similar to those before heating, which  
14 usually exists in  $\beta$ -phase (Fisher 1957, Pathak *et al.* 2007). Hence, no phase transformation may have  
15 occurred as no peaks of the  $\alpha$ -phase were detectable, possibly due to the rapid cooling rate (Goodman  
16 *et al.* 1981). Changes in thermoplasticized (ITP) peaks at 2850  $\text{cm}^{-1}$  and 2950  $\text{cm}^{-1}$ , which represent  
17 symmetric and asymmetric stretching of the  $\text{CH}_2$  respectively, were reversible (Fig.2-b). This may  
18 further support the unlikeliness of phase transformation (Pathak *et al.* 2006).

19  
20 Examining the effect of heat on gutta-percha revealed irreversible change in the peak at 350  $\text{cm}^{-1}$  in  
21 most brands (Figs.2-b, c). This peak represents the (C=C) bond located in the centre of gutta-percha's  
22 backbone (Pathak *et al.* 2006). The stretching mode of the same bond represented by the peak at 1670  
23  $\text{cm}^{-1}$  was also affected, which indicates that this bond is the most vulnerable upon heating and can be  
24 affected by temperature levels above 70 °C (Fig.2-b). This may agree with previous studies  
25 suggesting permanent alteration of gutta-percha due to chain cleavage after ageing or heating (Enoki  
26 *et al.* 2003, Silva *et al.* 2006). However, this cannot be correlated with oxidation, as Raman peaks  
27 representing C=O or C=O could not be detected. Thermal oxidation of gutta-percha was also  
28 suggested by Maniglia-Ferreira *et al.* (2008) producing (=C-H) bonds after consuming the (C=C)  
29 bonds in the polystyrene. Degradation of gutta-percha with heating was also reported using nuclear  
30 magnetic resonance imaging (Rodrigues *et al.* 2004), thermogravimetric analyses (Ferrante *et al.*  
31 2011), X-ray diffraction analyses and differential scanning calorimetry (Maniglia-Ferreira *et al.*  
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3 2013). Hence, upon heating gutta-percha, the clinicians should be aware of the temperature levels that  
4 should be used to avoid inducing such changes (Table-2).

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6  
7 Some of the changes in the Raman and FT-IR spectra of the epoxy resin-based sealer could be due to  
8 the setting reaction and breaking of the epoxy rings (Ellis 1993) (Fig.4-a, b). The irreversible drop in  
9 the FT-IR band at  $900\text{ cm}^{-1}$  (represents CO stretching in oxirane ring) may indicate accelerated setting  
10 of the sealer when heated above  $100\text{ }^{\circ}\text{C}$  (Gonzalez *et al.* 2012). However, irreversible changes in the  
11 Raman peaks at  $780\text{ cm}^{-1}$ ,  $2850\text{ cm}^{-1}$ ,  $2873\text{ cm}^{-1}$ , and  $2924\text{ cm}^{-1}$  (represent the  $\text{CH}_2$  group) can only be  
12 attributed to alterations in the structure of the resin. Such changes that appeared after heating the  
13 sealer above  $100\text{ }^{\circ}\text{C}$  agree with what was reported before (Viapiana *et al.* 2015, Camilleri 2015,  
14 Atmeh & AlShwaimi 2017) suggesting irreversible damage to the sealer's backbone upon heating.  
15 Therefore, the temperature level should not exceed  $100\text{ }^{\circ}\text{C}$  when epoxy resin-based sealers are used  
16 with warm vertical compaction (Table-2).

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19 Zinc oxide eugenol-based sealers set through an acid-base reaction forming a hard matrix of zinc  
20 eugenolate (Henry *et al.* 1955). This explains the drop in the peak at  $1190\text{ cm}^{-1}$  representing the COH  
21 group involved in the setting and the appearance of new peaks at  $1350\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  (Henry *et*  
22 *al.* 1955, Chowdhry *et al.* 2015, Khan *et al.* 2017) (Fig.4-c). Surprisingly, the spectra obtained after  
23 cooling the sealer differed from those obtained during heating (Fig.4-c, d). The Raman peaks that  
24 dropped after heating above  $125\text{ }^{\circ}\text{C}$  represent bonds in eugenol's benzene ring,  $\text{CH}_3$  and CO groups  
25 (Chowdhry *et al.* 2015). Hence, changes in these peaks could be due to molecular rearrangements in  
26 eugenol's structure that affects its stability and reactivity (McGraw *et al.* 1999, Turek & Stintzing  
27 2013). Changes in the FT-IR spectra were detectable at a lower temperature ( $100\text{ }^{\circ}\text{C}$ ), which may  
28 indicate even earlier changes. Although no changes were reported previously in this type of sealer  
29 (Viapiana *et al.* 2015), the present results clearly indicate irreversible changes upon heating and  
30 cooling, hence it may not be recommended to be used with warm compaction techniques (Table-2).

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33 Heating calcium silicate-based sealers had been investigated previously suggesting no effect on their  
34 chemical composition (Viapiana *et al.* 2015, Camilleri 2015, Atmeh & AlShwaimi 2017). However,  
35 water loss upon heating was reported using FT-IR (Viapiana *et al.* 2015) and thermogravimetric  
36 analysis (Atmeh & AlShwaimi 2017), and hence FT-IR was used here to examine the sealers and  
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3 verify the Raman results and investigate the change in water content. The FT-IR was able to detect the  
4 irreversible drop of BioRoot's FT-IR peaks at  $1650\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  that represent vibrational  
5 modes of the OH group in water (Fig.4-h). This confirms water loss above  $100\text{ }^{\circ}\text{C}$  through  
6 evaporation, which could not be reversed. The peak at  $3400\text{ cm}^{-1}$  also dropped in TotalFill that  
7 contains no water but may contain propylene glycol (Fig.4-f). The drop was reversible, however. Due  
8 to the increasing background noise in the Raman spectra of Totalfill above  $125\text{ }^{\circ}\text{C}$ , it was difficult to  
9 recognise changes (Fig.4-e). However, the spectra obtained after cooling were very similar to those  
10 before heating, indicating that all the changes that occurred during heating up to  $200\text{ }^{\circ}\text{C}$  were  
11 reversible. Further investigations about the effect of heat on the fluid uptake and integrity of calcium  
12 silicate based-sealers during heating are required considering their inorganic composition and nature,  
13 which render their setting based on water availability.  
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## 28 **Conclusions**

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30 The results strongly advocate the importance of identifying the actual temperature levels of  
31 endodontic heat carriers by practitioners, and the suitability of sealers to be used at the temperature  
32 achieved. All tested heat carriers reached temperature levels below  $60\text{ }^{\circ}\text{C}$  when used in cut-out mode,  
33 which is a safe level for most tested gutta-percha and all sealers. However, using some devices in  
34 continuous mode can produce higher temperature that may exceed the suggested safe levels. This may  
35 risk integrity of the root canal filling materials; hence clinicians should be cautious about heating  
36 durations. Zinc oxide-based sealers may not be recommended to be heated due to the detrimental  
37 effect of heat on its molecular structures. Tested epoxy resin and calcium silicate-based sealers bore  
38 heat below  $100\text{ }^{\circ}\text{C}$ , however higher temperature is not recommended.  
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55 providing the TotalFill® BC Sealer™.  
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3 **Conflict of Interest statement**  
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5 The authors have stated explicitly that there are no conflicts of interest in connection with this article.  
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For Peer Review

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*International Endodontic Journal* **35**, 527-35.

## Figure legends

**Figure 1:** The experimental set up for heat measurements of heat carriers.

**Figure 2:** The effect of heat on different brands of gutta-percha: **(a)** Characteristic Raman spectra of different brands of gutta-percha with peaks of interest labelled according to the peaks in the table below **(d)**. **(b)** The percentage of change in the intensity of Raman peaks (labelled in the table (d)) when heated up to 200 °C and after cooling compared with the intensity at 30 °C. The solid and dashed lines represent the highest and lowest percentage of change for the control peak (311 cm<sup>-1</sup>) respectively. **(c)** The effect of heat on the intensity of peaks of interest at each temperature level during heating gutta-percha from 30 °C to 200 °C. **PTU:** ProTaper Universal; **PTN:** ProTaper Next; **WO:** Wave One; **WG:** Wave One Gold; **TPI:** Thermo-plasticized Injectable; **STD:** Standardized gutta-percha.

**Figure 3:** Heat profiles of tested endodontic heat carriers and their specific set temperatures as indicated by the manufacturers. E&Q Master operated at 180 °C **(a)** and 230 °C **(b)** temperatures with automatic cut-out after 4s. Super Endo operated at 230 °C with a 4s cut-out **(c)** or in continuous mode for 30s **(d)**. System B operated at 200 °C with 4s cut-out mode **(e)** or continuous mode for 30s **(f)**. Heat profiles of the different tip diameters and tapers are shown for each device.

**Figure 4:** Real-time Raman and FT-IR spectra of different endodontic sealers obtained during heating from 25 °C to 200 °C (plotted from top to down) and after cooling (uppermost spectrum). **(a)(b)** Epoxy resin-based sealer (AH Plus). **(c)(d)** Zinc oxide eugenol-based sealer (Pulp Canal Sealer). **(e)(f)** Calcium silicate-based sealer (TotalFill BC Sealer. **(g)(h)** Calcium silicate-based sealer (BioRoot RCS). Peaks with changes in their intensity are marked with (\*).

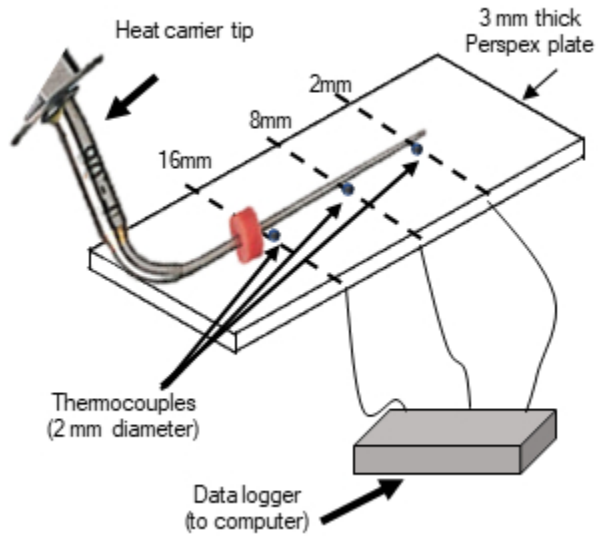
**Table 1** Safe temperature delivered by heat carriers:

Device	Manufacturer	Selected Temperature	Max. Temperature Delivered	Recommendation of use
E&Q Master	Meta Biomed	230 °C (Cut-out)	60 °C	- Heat generated does not exceed safe limit
SuperEndo B&L	B&L Biotech	230 °C (Cut-out) 230 °C (Cont.)	60°C 110 °C	- Heat generated does not exceed safe limit - Not to be used longer than 6 seconds
System-B	Sybrondental	200 °C (Cut-out) 200 °C (Cont.)	53 °C 66 °C	- Heat generated does not exceed safe limit

**Table 2** Safe temperature limits for tested obturation materials during heating:

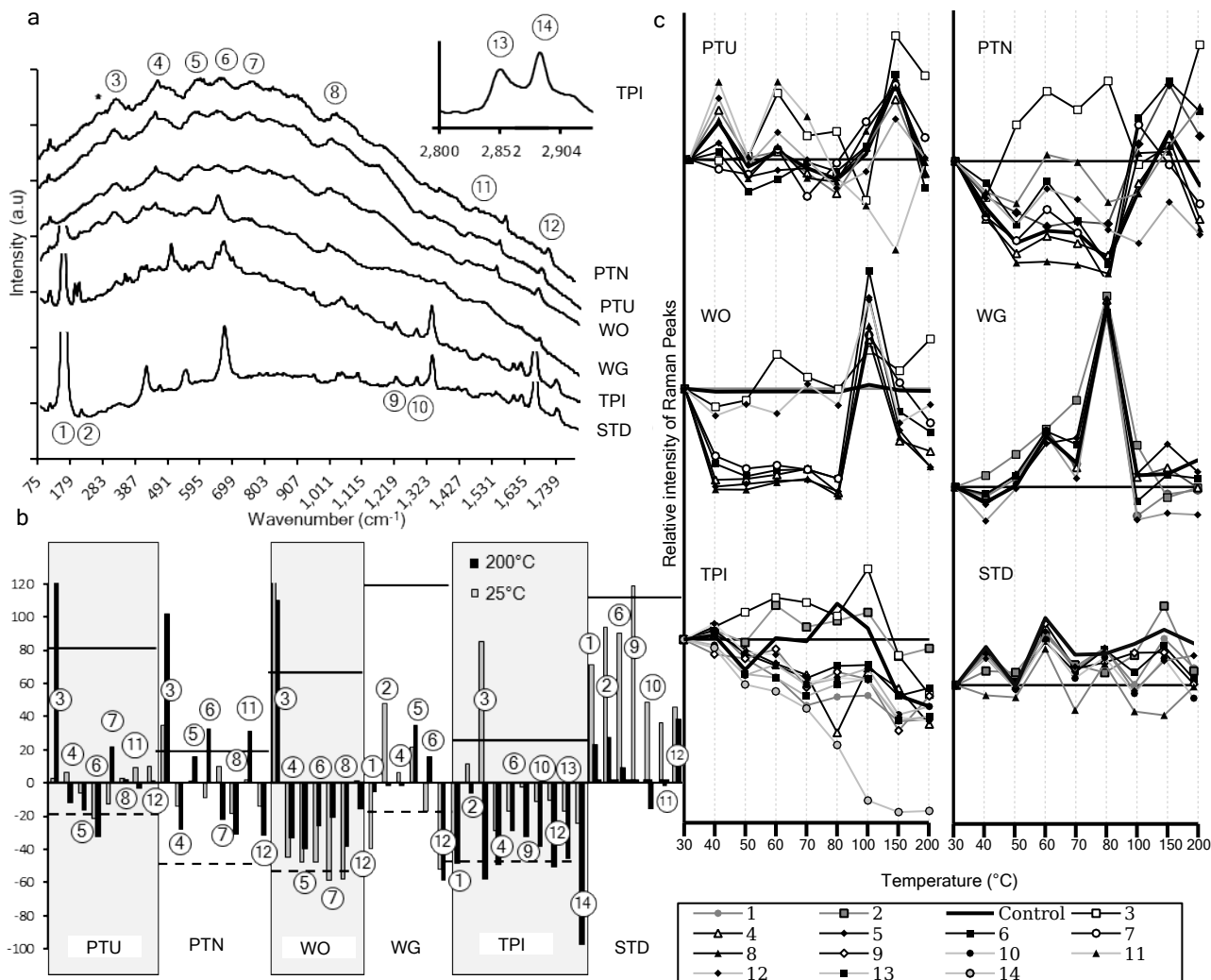
Material	Brand	Manufacturer	Safe heating temperature	Potential effects of heating beyond the safe temperature
Gutta-percha	ProTaper Universal	Dentsply	70 °C	Reversible changes above 70 °C
	ProTaper Next	Dentsply	70 °C	Irreversible changes involving gutta-percha's backbone (C=C bonds)
	Wave One	Dentsply	50 °C	Irreversible changes involving gutta-percha's backbone (C=C bonds)
	Wave One Gold	Dentsply	100 °C	Irreversible changes involving gutta-percha's backbone (C=C bonds)
	Thermoplasticized gutta-percha	Sure Dent	70 °C	Irreversible changes involving gutta-percha's backbone (C=C bonds)
	2% standardized points	Sure Dent	80 °C	Irreversible changes involving gutta-percha's backbone (CH <sub>2</sub> group)
	Sealers	AH Plus	Dentsply	100 °C
Pulp Canal Sealer		Kerr	Not recommended to heat	Changes detectable upon cooling, not recommended to be used with warm obturation
TotalFill BC Sealer		FKG	100 °C	Reversible changes above 125 °C
BioRoot RCS		Septodont	100 °C	Water loss above 100 °C

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The experimental set up for heat measurements of heat carriers.

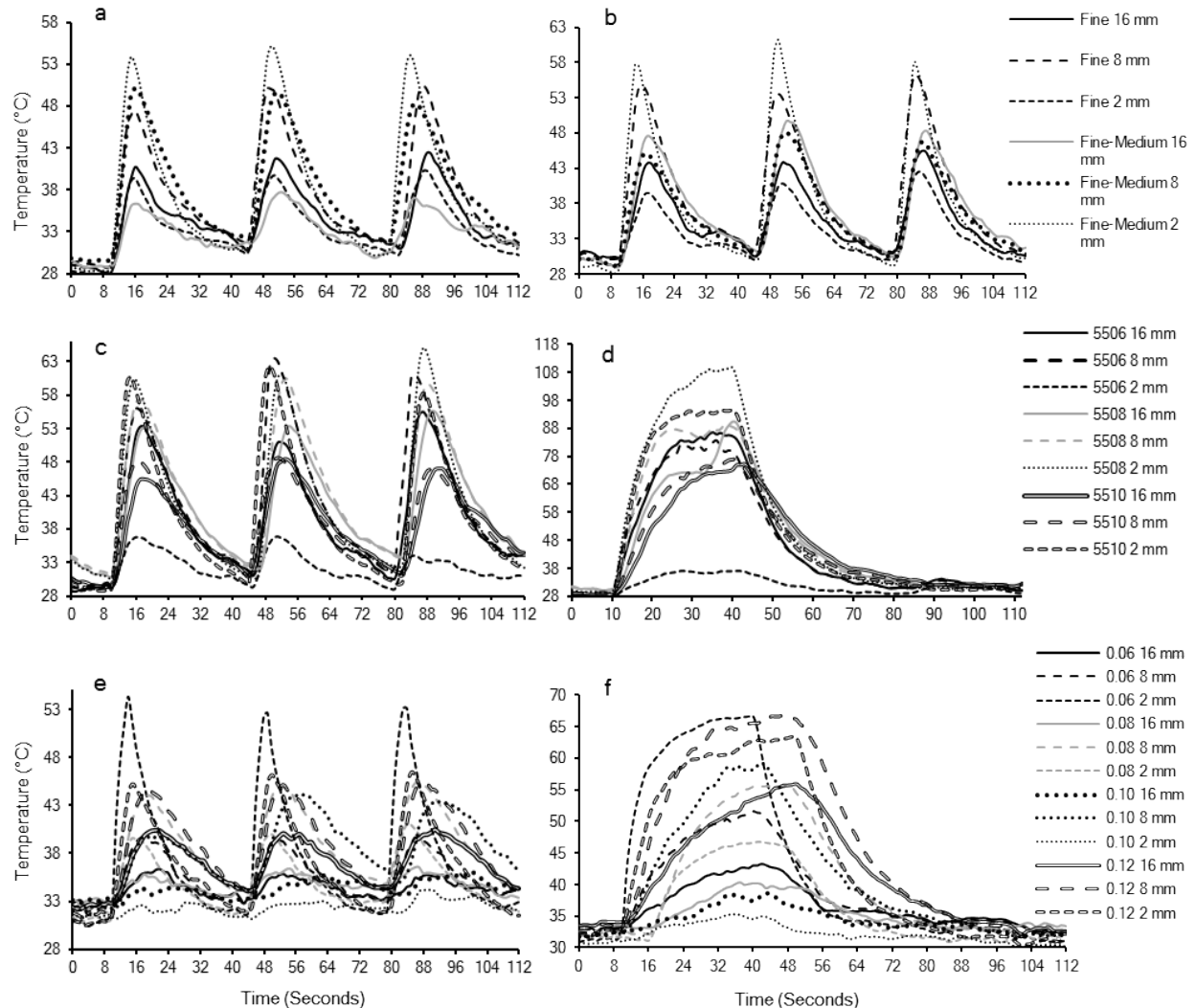
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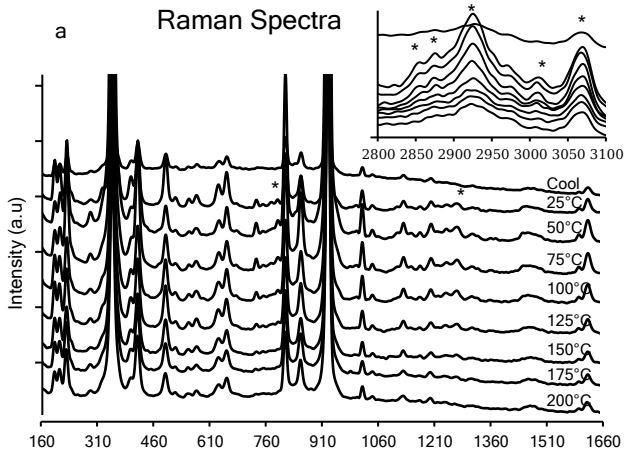
Peak No.	Raman Peak	Assignment	Peak No.	Raman Peak	Assignment
1	146 cm <sup>-1</sup>	C-C torsion <sup>(1)</sup>	8	1024 cm <sup>-1</sup>	CH <sub>3</sub> rocking, C-C stretching <sup>(2)</sup>
2	201 cm <sup>-1</sup>	CH <sub>3</sub> torsion <sup>(2)</sup>	9	1179 cm <sup>-1</sup>	CH <sub>3</sub> wagging <sup>(2)</sup>
3	350 cm <sup>-1</sup>	C=C torsion <sup>(3)</sup>	10	1284 cm <sup>-1</sup>	CH <sub>2</sub> twisting <sup>(2)</sup>
4	444 cm <sup>-1</sup>	C-C out of plane bending <sup>(2)</sup>	11	1440 cm <sup>-1</sup>	CH <sub>2</sub> deformation <sup>(2)</sup>
5	570 cm <sup>-1</sup>	C-C in plane bending <sup>(2)</sup>	12	1670 cm <sup>-1</sup>	C=C stretching <sup>(3)</sup>
6	643 cm <sup>-1</sup>	C-C in plane bending <sup>(2)</sup>	13	2851 cm <sup>-1</sup>	C-H stretching <sup>(3)</sup>
7	740 cm <sup>-1</sup>	CH <sub>2</sub> rocking, CH out of plane stretch <sup>(2)</sup>	14	2885 cm <sup>-1</sup>	C-H stretching <sup>(3)</sup>
Stndrd	105 cm <sup>-1</sup>	Barium (Sulfate): A1g(Ba) + Eg(Ba) <sup>(4)</sup>	Control	311 cm <sup>-1</sup>	Zinc Oxide- E <sup>2</sup> mode <sup>(5)</sup>

<sup>1</sup>Pathak et al. 2007; <sup>2</sup>Arjunan et al. 2001; <sup>3</sup>Pathak et al. 2006; <sup>4</sup>Sun & Chen 2015; <sup>5</sup>Dong et al. 2006.





Raman Spectra



FTIR Spectra

